Fischer Carbene Complexes in Heterocyclic Synthesis. Selective Cycloaddition Reactions to 2-Aza-1,3-butadienes

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A structurally diverse set of Fischer carbene complexes are reacted with substituted 3-[(trimethylsilyl)oxy]-2-aza-1,3-butadienes **1,** yielding 5- to 7-membered nitrogen-containing heterocycles in a selective manner. Aryl and heteroarylmetal carbenes **2** undergo [4 + 1] cycloaddition with **1** leading to pyrrolidone derivatives **3**−**5** or **6**−**9**, depending on the C1-substituent of **1**. The [(trimethylsilyl)ethynyl]carbene **10a** gives rise to metal-containing and metal-free [4 + 2] cycloadducts **11** and **12**, respectively, whereas the (phenylethynyl)carbene **10b** furnishes azafluorenones **13** by a tandem [4 + 2] cycloaddition/pentaannulation process. In the case of alkenyl carbene complexes **14** the regioselective [4 + 3] cycloaddition is the only observed transformation. Thus, their reaction with the phenyl-substituted azadiene **1d** resulted in the formation of a ≈1:1 mixture of diastereoisomers **15** and **16**, whereas in the case of the *tert*-butyl-substituted azadiene **1c** the *cis*-diastereoisomers **15** are selectively formed. This heptaannulation is proposed to occur by a cyclopropanation/aza-Cope rearrangement.

Introduction

Since their discovery in 1966 by Fischer,[1] stabilized Fischer carbene complexes of group 6 have been recognized to play an important role in the construction of a variety of 3- to 7-membered carbocyclic rings and acyclic compounds as well.[2] For instance, reactions involving the carbene ligand of α,β-unsaturated complexes, as the activated two-electron system, have permitted a number of [2+2][2d,3] and [4 + 2][4] cycloadditions as well as 1,3-dipolar cycloadditions to be achieved[5] On the other hand, the reactions occurring at the metal center are doubtless more characteristic for these systems, and important carbocyclizations of the type [2 + 1],[6] [2 + 1 + 1],[7] [4 + 1],[8] [3 + 2],[9,10] [3 + 2 + 1],[9] [4 + 2 + 1 − 2],[11] [4 + 2 + 1],[12] and [4 + 3][13] have been reported quite frequently in the last years. The flexibility of these organometallic reagents toward organic substrates has also made them useful tools in natural products synthesis.[14]

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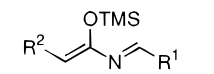
On the contrary, the reactivity of this type of metal carbene complexes toward heteroatom-containing substrates has been much less studied. Thus, reports dealing with the usefulness of Fischer carbene complexes in heterocyclization reactions are not as numerous compared to those mentioned for the all carbon counterparts. In this context, imine derivatives represent in various ways attractive substrates to be tested. Apart from the well-known β-lactam ring formation via photochemical [2 + 1 + 1] cycloadditon,[7a] isolated examples comprising [3 + 2],[5,15] [4 + 1],[16] and [3 + 3][17] cycloadditions between simple and α,β-unsaturated imines and Fischer carbene complexes have appeared.

Because of our long-standing interest in the chemistry of azadiene derivatives,[18] we decided to initiate a study of their reactivity toward Fischer carbene complexes in order to get more insight into the behavior of these metal complexes and to develop novel methodologies in heterocyclic synthesis as well. Thus, we discovered that the azepine skeleton is readily formed from α,β-unsaturated Fischer carbene complexes and 1-azadiene (α,β-unsaturated imine) derivatives following a sequence that involves (i) 1,2-nitrogen addition to the metal−carbon bond and (ii) 1,2-metal migration-promoted cyclization via C_β-(carbene complex fragment)−C_β(unsaturated imine fragment) coupling.[19] Moreover, on working with these imine derivatives we have been able to perform the first [4 + 2] cycloaddition of Fischer carbenes with heterodienes.[20,21]

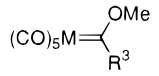
These achievements prompted us to extend this study to other types of heterodienes and herein we want to disclose the results obtained when different types of group 6 Fischer carbene complexes were reacted with readily available electron-rich 2-azadienes.[22] Specifically, it is shown that aryl **(2)**, alkynyl **(10),** and alkenyl **(14)** carbene complexes react with 3-(trimethylsiloxy)-2-aza-1,3-butadienes **(1)** to afford selectively [4 + 1], [4 + 2], and [4 + 3] cycloadducts, respectively.

Results and Discussion

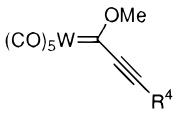
Throughout this work the following carbene complexes and 2-azadienes have been employed.



	R^1	R^2
1a	2-furyl	H
b	4-$MeOC_6H_4$	H
c	*t*-Bu	H
d	Ph	H
e	*t*-Bu	Me

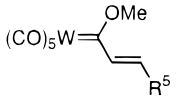


	M	R^3
2a	Mo	Ph
b	W	Ph
c	W	2-furyl



	R^4
10a	TMS
b	Ph

(TMS = $SiMe_3$)



	R^5
14a	Ph
b	2-furyl

[4 + 1] Cycloaddition of 2-Azadienes (1) and Fischer Carbene Complexes (2). We initiated our work studying the cyclization of aryl(methoxy)methylene complexes **2** as the simplest model. Thus, the reaction of molibdenum complex **2a** with 3-(trimethylsiloxy)-2-azabutadienes **1a,b** in THF at room temperature furnished a reaction crude consisting of a diastereomeric mixture of the [4 + 1] cycloadducts **3** and **4** in more than 85% yield (**3a**/**4a** = 3:1; **3b**/**4b** = 3:2).[23] Column chromatography allowed **3a** (57%) and **4a** (21%) to be isolated as well as the mixture **3b** + **4b,** which could not be separated, to be purified (Scheme 1; Table 1, entries 1 and 2). The relative stereochemistry of **3** and **4** could be ascertained by means of nuclear Overhauser enhancement experiments. On the other hand, the reaction between the tungsten complex **2b** and the 2-azadiene **1b** did not lead to the expected adducts **3b** and **4b**, but further elimination of methanol and formation of the pyrrolidone **5** (87% yield) took place exclusively (Table 1, entry 3).

Quite intriguing was the finding that a diastereomeric mixture of pyrrolidinones **6** and **7** (15:1 for **6a**/**7a**, 5:2 for **6b**/**7b**), where 1,2-migration of the methoxy group had occurred, were formed when 1-*tert*-butyl-3-(trimethylsiloxy)-2-azadiene (**1c)** was reacted with complexes **2b,c** (Scheme 2; Table 1, entries 4 and 5). Column chromatography of the mixture of cycloadducts **6** and **7** resulted in the isolation of stereochemically pure compounds **6** (**6a**, 92%; **6b**, 60%), while the stereoisomers **7** suffered methanol elimination giving the unsaturated adducts **8** (**8a**, not isolated; **8b**, 23%). Furthermore, aqueous hydrolysis (12 M HCl/THF) of the crude mixture (**6** + **7**) led to the α,β-unsaturated pyrrolidones **9a,b** (78−90% from **1c**). The constitution and relative configuration of the unexpected cycloadducts **6** were determined by 2D HMBC NMR spectra,[24] which established the connectivity, and nuclear Overhauser enhancement experiments done on compound **6a**.

A mechanistic proposal for both cyclopentaannulation reactions is given in Scheme 3. In light of the known reactivity of Fischer carbene complexes toward activated alkenes, the formation of the [4 + 1] cycloadducts **3** and

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(21) The reaction of alkenyl imidates and alkynyl Fischer carbene complexes has been very recently reported to afford Michael-type adducts and variable amounts of pyrrole and azetidine cycloadducts: Aumann, R.; Fröhlich, R.; Zippel, F. *Organometallics* **1997**, *16*, 2571.

(22) For representative, very recent examples, see: (a) Ghosez, L.; Bayard, P.; Nshimyumukiza, P.; Gouverneur, V.; Sainte, F.; Beaudegnies, R.; Rivera, M.; Frisque-Hesbain, A.-M.; Wynants, C. *Tetrahedron* **1995**, *51*, 11021. (b) Gouverneur, V.; Ghosez, L. *Tetrahedron* **1996**, *52*, 7585.

(23) Throughout this paper all the cycloadducts containing the *O*-silyl/*N*-silyl imidate funtion, which are initially formed from azadienes **1**, are not isolated but they undergo protonolysis to the amide function during workup.

(24) Bax, L; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093.

Scheme 1

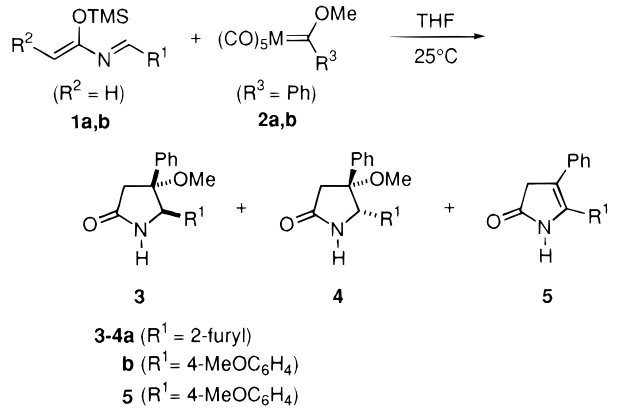
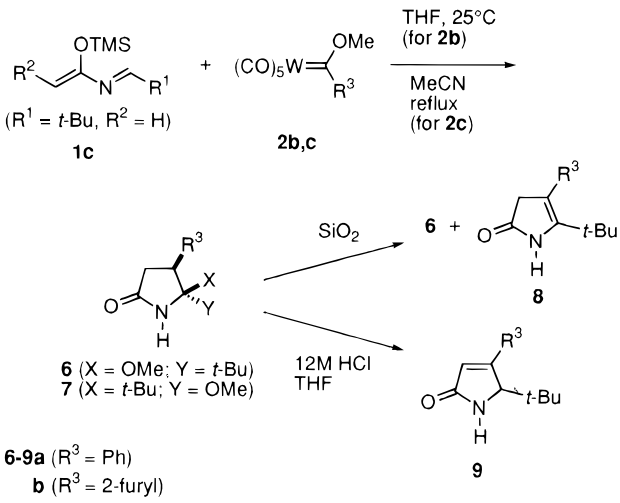


Table 1. Cycloadducts 3−6, 8, 9 Obtained from 1 and 2 (Schemes 1 and 2)

entry	M	R^1	R^3	products (yield)[a]
1	Mo	2-furyl		**3a** (57%), **4a** (21%)
2	Mo	4-MeO-C_6H_4		**3b** + **4b** (84%)[b]
3	W	4-MeO-C_6H_4		**5b** (87%)
4	W		Ph	**6a** (92%), **9a** (90%)[c]
5	W		2-furyl	**6b** (60%), **8b** (23%), **9b** (78%)[c]

[a] Yields after column chromatographic purification. [b] As a 3:2 mixture that could not be separated by column chromatography. [c] Overall yield after hydrolysis of the crude mixture (**6** + **7**).

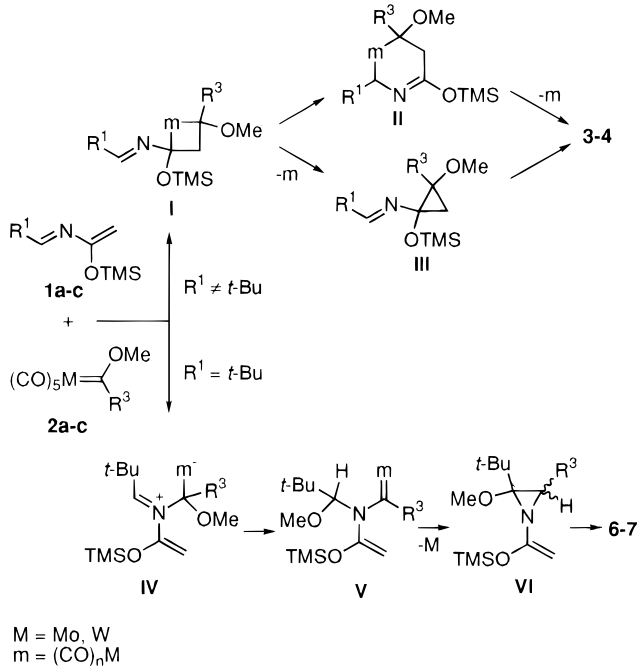
Scheme 2



4 can be explained by initial [2 + 2] cycloaddition of the metal carbene **2** to the electron-rich carbon−carbon double bond of azadiene **1** to form the intermediate metallacyclobutane **I**. The transformation of this species into the final adducts could follow two pathways: (i) [1,3]-metal migration to form a 1-metalla-3-azacyclohexene species **II** and reductive elimination[25] and (ii) reductive metal elimination followed by 3- to 5-membered ring expansion of the resulting *N*-cyclopropylimine intermediate **III**.[26]

Concerning the formation of the [4 + 1] cycloadducts **6** and **7**, particularly the [1,2]-rearrangement of the

Scheme 3



methoxy group, the following three-step sequence might be invoked: (i) nucleophilic *N*-attack to the carbene carbon to give **IV**, (ii) [1,3]-OMe migration giving rise to the amino carbene complex **V**, and (iii) insertion of the C_β-H into the metal carbene and reductive elimination of "$(CO)_nW$" to form vinylaziridine **VI**, which would suffer regioselective ring expansion to the 5-membered heterocycles **6** and **7**. All of these steps have precedents in the literature of Fischer carbene complexes. Thus, whereas the formation of zwitterionic species of type **IV** has been well-established for different imine derivatives,[19,27] the [1,3]-OAc migration has been proposed in the reaction of simple imines and (acyloxy)benzylidene complexes.[28] Although the activation of a C−H bond is a quite rare process in the case of Fischer carbenes, a few examples showing its feasibility have been reported in recent years.[29]

[4 + 2] Cycloaddition of 2-Azadienes (1) and Alkynyl Fischer Carbene Complexes (10). Unsaturated Fischer carbene complexes, particularly alkynyl derivatives, are excellent dienophile partners in the classical Diels−Alder reaction. Therefore, we investigated their reactivity toward 2-azadienes **1**, a type of heterodiene with high capability to cycloadd to electron-poor alkenes (alkynes) and frequently utilized in synthesis of interesting molecules containing the pyridine ring (Scheme 4; Table 2, entries 1 and 2). First, (trimethylsilyl)ethynyl carbene **10a** was allowed to react with 2-azadiene **1c** (R^1 = *t*-Bu) at room temperature in THF to afford the pyridone derivative **11a** in 92% yield after column chromatography purification. Further heating at 60 °C resulted in removal of the metal fragment by

(25) This reaction pathway has been proposed by Hegedus et al. in the case of the [4 + 1] cycloaddition of [(dimethylamino)carbene]-pentacarbonylchromium(0) with methyl *E*-hexa-2,4-dienoate; see ref 8a.

(26) For cyclopropylimine−pyrroline rearrangements, see: (a) Hudlicky, T.; Reed, J. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 5, p 941. (b) Reference 16a.

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(29) (a) Reference 8c. (b) Barluenga, J.; Rodríguez, F.; Vadecard, J.; Bendix, M.; Fañanás, F. J.; López-Ortiz, F. *J. Am. Chem. Soc.* **1996**, *118*, 6090. (c) Wang, S. L. B.; Su, J.; Wulff, W. D.; Hoogsteen, K. *J. Am. Chem. Soc* **1992**, *114*, 10665.

Scheme 4

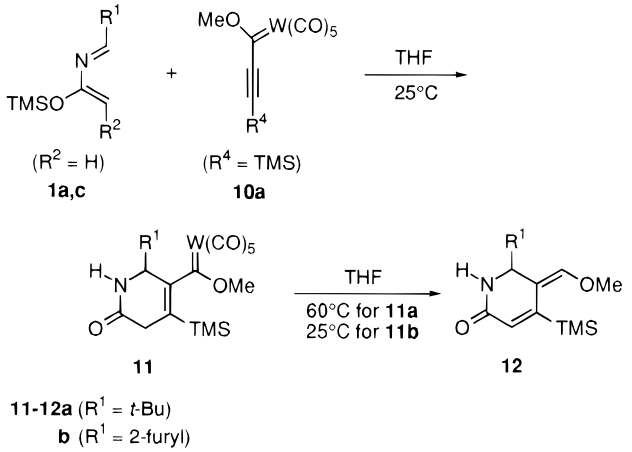
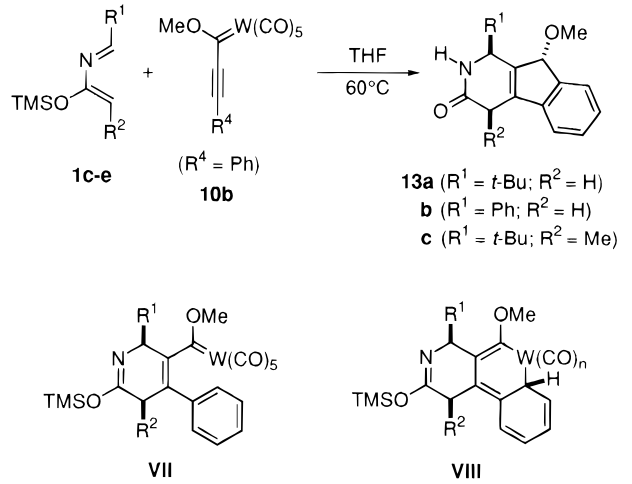


Table 2. Cycloadducts 11−13 Obtained from 1 and 10 (Schemes 4, 5)

entry	R^1	R^2	products (yield)[a]
1	*t*-Bu		**11a** (92%), **12a** (82%)
2	2-furyl		**12b** (71%)[b]
3	*t*-Bu	H	**13a** (76%)[c]
4	Ph	H	**13b** (84%)[c]
5	*t*-Bu	Me	**13c** (62%)[c]

[a] Yields after column chromatographic purification. [b] Overall yield from **1a** and **10a** (**11b** not isolated). [c] Recrystallized from methanol; mp (°C) 183−185 (**13a**), 204−206 (**13b**), 199−201 (**13c**).

Scheme 5



[1,5]-H shift and reductive elimination yielding **12a** (82% yield) as the *E*-isomer according to NOE experiments. In the case of starting with azadiene **1a** (R^2 = 2-furyl), the corresponding cycloadduct **11b** could not be isolated, but metal-free pyridone **12b** was directly obtained in 71% yield after purification.

Moreover, when the (phenylethynyl)carbene complex **10b** was used, a double cyclization process took place (Scheme 5; Table 2, entries 3−5). Thus, the treatment of tungsten complex **10b** with 2-azadienes **1c**−**e** in THF at 60 °C followed by column chromatography purification resulted in the stereoselective formation of 2-azafluorenones **13a**−**c** in good yields. The whole transformation most likely involves intermediates **VII** and **VIII**. The former represents the expected [4 + 2] cycloadduct which would undergo further selective electrocyclic ring closure through the 1-metalla-1,3,5-triene moiety leading to the metallacycle **VIII** (W−C bond formation from the less encumbered face). Last, the suprafacial [1,5]-hydrogen shift and reductive elimination would account for the conversion of **VIII** into **13**.[30] The stereoselectivity found for both cyclizations—[4 + 2] cycloaddition and cyclopentaannulation—was unambiguously proven by an X-ray structure determination performed on compound **13a**.[31]

Scheme 6

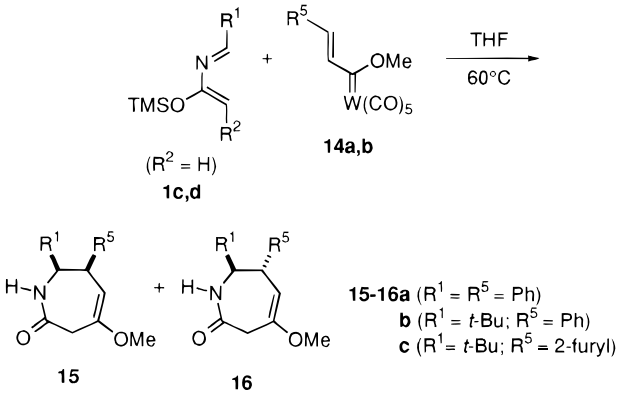
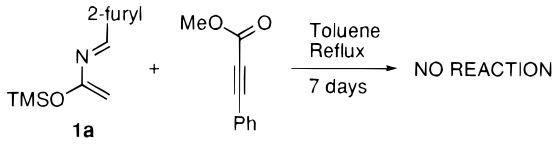


Table 3. Azepinones 15 and 16 Obtained from 1 and 14 (Scheme 6)

compd	R^1	R^5	yield (%)[a]	mp (°C)[b]
15a	Ph	Ph	42	135−137
16a	Ph	Ph	38	136−138
15b	*t*-Bu	Ph	94	144−146
15c	*t*-Bu	2-furyl	88	139−141

[a] Yields after column chromatographic purification. [b] Recrystallized from methanol.

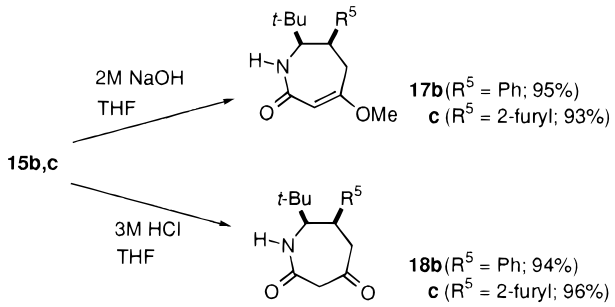
Finally, we decided to compare the reactivity of tungsten alkynylcarbene complexes as electron-poor dienophiles with that of the acetylenic ester analogues because of the isolobal relation between a d^6-metal pentacarbonyl fragment and an oxygen atom. In full agreement with previous studies for carbodienes,[32] we also found that the metal carbene substituted alkynes are much more reactive toward azadienes **1** since the attempted cycloaddition between **1a** and methyl phenylpropiolate in refluxing toluene for 7 days resulted only in the recovery of the starting adducts (eq 1).



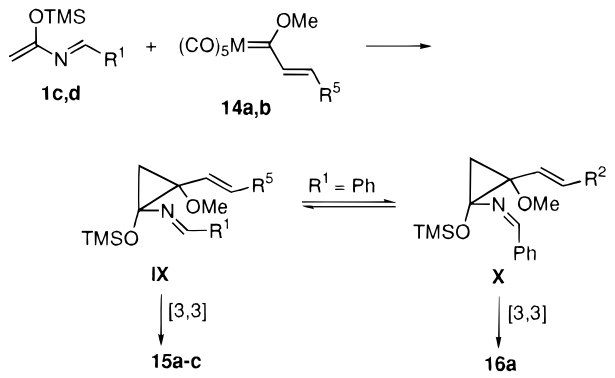
[4 + 3] Cycloaddition of 2-Azadienes (1) and Alkenyl Fischer Carbene Complexes (14). On thinking about other reaction pathways of Fischer carbene complexes, we turned our attention to alkenylcarbene complexes, since they are known to be more prone to undergo higher order cycloadditions, e.g. the [4 + 3] cycloaddition, than the above studied alkynyl derivatives (Scheme 6, Table 3). Thus, azadiene **1d** (R^1 = Ph) was first reacted with alkenylcarbene **14a** at 60 °C in THF to yield a nearly 1:1 mixture of *cis*- and *trans*-azepinone derivatives **15a** and **16a**, respectively. Column chromatographic separation of this mixture provided both stereoisomers in a pure

(30) For previous examples from our laboratory, see ref 4e, p 20.
(31) García-Granda, S.; Santiago, R.; Suárez-Sobrino, A.; Santamaría, J. To be published.
(32) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983,** *105*, 6726; *J. Am. Chem. Soc* **1984**, *106*, 7565.

Scheme 7



Scheme 8



form (**15a**, 42%; **16a**, 38%). However, the cycloaddition became totally stereoselective in favor of the *cis*-isomer when the phenyl group in the starting azadiene was replaced with the *tert*-butyl group. In this case, the reaction of 2-azadiene **1c** (R^1 = *t*-Bu) with carbene complexes **14a,b**, under the same reaction conditions, led to excellent yields (88−94%) of the corresponding [4 + 3] *cis*-cycloadducts **15b,c** after chromatographic purification. The relative stereochemistry of the resulting cycloadducts **15** and **16** could not be established by NOE experiments because of signals overlapping, but it was necessary to effect previously a chemical transformation (vide infra).

Under basic catalysis, the β,γ-unsaturated ϵ-lactams **15b,c** were tautomerized to the conjugated derivatives **17b,c** (Scheme 7), whose stereochemistry was clearly confirmed at this stage by NOE experiments on C6−H/C7−H. In the same way, **15b,c** could be readily hydrolyzed with aqueous acid to azepin-2,4-dione derivatives **18b,c**.

Although a definitive reaction course cannot be put forward, we think that a mechanistic proposal might be given on the light of the existing precedents for heptaannulation of Fischer carbene complexes (Scheme 8). This type of cyclization has been shown to involve two pathways depending on the type of organic substrate: (i) tandem cyclopropanation/Cope rearrangement of 1,2-divinylcyclopropanes[13] and (ii) consecutive nucleophilic attack at the carbene center/1,2-$M(CO)_5$ shift-promoted cyclization.[19] The former is assumed for electron-rich carbodienes, while the latter operates in the case of various types of 1-azadienes, the stereochemical reaction course being opposite to each other. Primarily on the basis of the stereochemical outcome for the C6−C7 coupling, the formation of *cis*-cycloadducts **15** would likely arise from cyclopropanation of the electron-rich C3−C4 double bond of 2-azadienes **1** to generate cyclopropane species **IX** followed by aza-Cope rearrangement. Furthermore, the presence of the *trans*-cycloadduct **16a** (R^1 = Ph) might be rationalized if the [3,3]-rearrangement is preceded by partial isomerization of the *anti*-cyclopropylimine intermediate **IX** to the *syn*-derivative **X**.[33,34]

Conclusions

In summary, the synthetic utility of Fischer carbene complexes toward 2-azadienes has been studied for the first time. Each class of carbene complexes shows a differential behavior, giving 5- to 7-membered nitrogen heterocycles in good to excellent yields. Thus, methoxyarylmethylene complexes undergo [4 + 1] cycloaddition, providing 2-pyrrolidones. (Methoxyalkynyl)tungsten complexes behave as activated dienophiles, affording regioselectively new [4 + 2] heterocycloadducts that still contain the metal carbene functionality, thus allowing on occasion the elaboration of them into more complex structures. Last, (methoxyalkenyl)tungsten complexes produced regioselectively substituted azepinones; this [4 + 3] cycloaddition involves coupling of two C−C−C and C−C−N−C fragments and represents a novel entry into the azepine skeleton.[35,36]

Experimental Section

General Methods. Melting points are uncorrected. IR spectrum was recorded on a FT IR instrument ^{1}H NMR spectra were recorded at 200 or 300 MHz with TMS as internal standard. ^{13}C NMR spectra were recorded at 50 or 75 MHz. ^{13}C NMR multiplicities were determined by DEPT experiments. 2D HMBC[24] experiments were determined on a 400 MHz spectrometer. Unless otherwise noted, NMR experiments were run in $CDCl_3$. High-resolution mass spectra (HRMS) were determined at an ionizing voltage of 70 eV. Column chromatography was performed with silica gel (230−400 mesh) by standard flash chromatographic techniques.[37]

Materials. THF was treated with sodium and distilled over sodium. CH_3CN was distilled from CaH_2. The preparations of the starting 2-azadienes **1**[22b] and Fischer carbene complexes **2**,[1] **10**,[38] and **14**[39] have been previously described.

[4 + 1] Cycloaddition of 2-Azadienes 1a,b and Fischer Carbene Complexes 2a,b. Synthesis of 3−5. A mixture

(33) Previous reports of NMR studies on aldimines have revealed that variable amounts of the *Z*-isomer are in equilibrium with the *E*-isomer in the case of *C*-aryl, *N*-alkyl aldimines even at room temperature. (a) Tennant, G. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: New York, 1979; Vol. 2, p 396. (b) Bjorgo, J.; Boyd, D. R.; Watson, C. G.; Jennings, W. B.; Jerina, D. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1081.

(34) The participation of the second mechanism, consisting of nucleophilic attack of the C4 of **1d** (R^2 = Ph) onto the carbene carbon of **14** and cyclization, would also account for the formation of the *trans*-cycloadduct **16a**. However, this choice can be in principle ruled out since the more nucleophilic azadiene **1c** (R^2 = *t*-Bu) gives none of the corresponding **16b,c**.

(35) Reviews on azepines, see: (a) Evans, P. A.; Holmes, A. B. *Tetrahedron* **1991**, *47*, 9131. (b) Hassenrück, K.; Martin, H. D. *Synthesis* **1988**, 569. (c) Smalley, R. K. In *Comprehensive Heterocyclic Chemistry*; Lwowski, W., Ed.; Pergamon: Oxford, 1984; Vol. 7, p 491. For recent syntheses of 2-azepinones, see: (d) Robl, J. A.; Cimarusti, M. P. *Tetrahedron Lett.* **1994**, *35*, 1393. (e) Robl, J. A.; Cimarusti, M. P.; Simpkins, L. M.; Weller, H. N.; Pan, Y. Y.; Malley, M.; DiMarco, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 2348. (f) Evans, P. A.; Holmes, A. B.; Russell, K. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3397. (g) Evans, P. A.; Holmes, A. B. *Tetrahedron* **1991**, *47*, 9131.

(36) Using chromium carbene complexes resulted in all cases in the formation of complex mixtures of unidentified products. In the same way, all attempts to carry out the [4 + 3] cycloaddition with α,β-unsaturated molybdenum carbene complexes, e.g. pentacarbonyl[(1-cyclohexenyl) methoxymethylene]molybdenum(0), at 25 and 60 °C led to recovery of the starting materials and to products derived from decomposition of the carbene complex, respectively.

(37) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(38) Auman, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.

(39) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Mejiere, A. *Chem. Ber.* **1992**, *125*, 2923.

of azadiene **1** (1mM) and Fischer carbene complex **2a,b** (1mM) in 50 mL of THF was stirred for 15 h at 25 °C. Then, the solvent was removed under reduced pressure and the residue purified by column chromatography (hexane/ethyl acetate, 1:1).

Compounds **3a**, **4a,** and **5** were isolated as pure solids. Compounds **3b** and **4b** were isolated as a 3:2 unseparable mixture.

***(4R,5S/4S,5R)*-5-(2-Furyl)-4-methoxy-4-phenylpyrrolidin-2-one (3a):** yield 57%; mp 142−144 °C; ^{1}H NMR δ 2.95 (d, 1H, J = 16.5 Hz), 3.0 (s, 3H), 3.1 (d, 1H, J = 16.5 Hz), 4.75 (s, 1H), 6.4 (m, 2H), 6.5 (brs, 1H), 7.2−7.5 (m, 6H); ^{13}C NMR δ 175.0 (s), 150.5 (s), 142.8 (d), 140.8 (s), 128.7 (d), 128.2 (d), 126.2 (d), 110.4 (d), 109.0 (d), 84.1 (s), 62.9 (d), 52.6 (q), 38.8 (t); HRMS *m/z* calcd for $C_{15}H_{15}NO_3$ 257.1052, found 257.1053. Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found C, 70.15; H, 5.74; N, 5.51.

(4*R*,5*R*/4*S*,5*S*)-5-(2-Furyl)-4-methoxy-4-phenylpyrrolidin-2-one (4a): yield 21%; mp 146−148 °C; ^{1}H NMR δ 2.85 (d, 1H, J = 14.6 Hz), 3.1 (s, 3H), 3.1 (d, 1H, J = 14.6 Hz), 4.9 (s, 1H), 5.9 (m, 1H), 6.1 (m, 1H), 6.3 (brs, 1H), 7.0−7.5 (m, 6H); ^{13}C NMR δ 175.1 (s), 150.4 (s), 142.2 (d), 136.7 (s), 128.0 (d), 127.7 (d), 126.7 (d), 110.0 (d), 108.1 (d), 87.0 (s), 64.0 (d), 51.5 (q), 36.1 (t); HRMS *m/z* calcd for $C_{15}H_{15}NO_3$ 257.1052, found 257.1064. Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found C, 70.09; H, 5.94; N, 5.36.

***(4R,5S/4S,* 5*R*)-4-Methoxy-5-(4-methoxyphenyl)-4-phenylpyrrolidin-2-one (3b) and (4*R*,5*R*/4*S*,5*S*)-4-Methoxy-5-(4-methoxyphenyl)-4-phenylpyrrolidin-2-one (4b):** global yield 84%;^{1}H NMR (C_6D_6) δ 2,7 and 2.8 (s, 3H), 2.6−3.0 (m, 2H), 3.2 and 3.3 (s, 3H), 4.4 and 4.9 (s, 1H), 6.5−8.3 (m, 10H); ^{13}C NMR (C_6D_6) δ 175.7 and 175.6 (s), 159.9 and 159.4 (s), 140.6 and 138.3 (s), 130.3 and 129.3 (d), 128.6 and 128.4 (s), 128.3 and 127.9 (d), 127.8 and 127.7 (d), 127.5 and 127.0 (d), 113.4 (d), 87.8 and 84.9 (s), 70.0 and 69.6 (d), 54.6 and 54.5 (q), 51.8 and 51.3 (q), 38.8 and 38.2 (t); HRMS *m/z* calcd for $C_{18}H_{19}NO_3$ 297.1365, found 297.1373. Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found C, 72.55; H, 6.56; N, 4.81.

5-(4-Methoxyphenyl)-4-phenyl-1,3-dihydro-2*H*-pyrrol-2-one (5): yield 87%; mp 158−160 °C; ^{1}H NMR δ 3.5 (s, 2H), 3.8 (s, 3H), 6.7−7.5 (m, 9H), 8.9 (brs, 1H); ^{13}C NMR δ 178.4 (s), 159.9 (s), 135.9 (s), 134.6 (s), 129.1 (d), 128.3 (d), 127.0 (d), 126.3 (d), 123.2 (s), 114.4 (d), 112.5 (s), 55.2 (q), 41.2 (t); HRMS *m/z* calcd for $C_{17}H_{15}NO_2$ 265.1103, found 265.1107. Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found C, 76.81; H, 5.74; N, 5.41.

[4 + 1] Cycloaddition of 2-Azadiene 1c and Fischer Carbene Complexes 2b,c. Synthesis of 6, 8, and 9. A mixture of azadiene **1c** (1 mM) and Fischer carbene complex **2b,c** (1 mM) was stirred for 15 h in 50 mL of THF at 25 °C (for **2b**) or in 50 mL of CH_3CN at 80 °C (for **2c**). Then, the solvent was removed under reduced pressure and the crude mixture of **6** and **7** subjected to the following treatments: (A) Column chromatography (hexane/ethyl acetate 1:1) (compounds **6a**, **6b,** and **8b** were isolated by this procedure) and (B) treatment with 12 M HCl (five drops) in 30 mL of THF for 30 min at 25 °C; further extraction with ether (3 × 20 mL), solvents removal, and purification of the residue by column chromatography (hexane/ethyl acetate, 1:1) gave compounds **9**.

(4*R*,5*R*/4*S*,5*S*)-5-*tert*-Butyl-5-methoxy-4-phenylpyrrolidin-2-one (6a): yield 92%; mp 124−126 °C; ^{1}H NMR (C_6D_6) δ 1,1 (s, 9H), 2,6 (m, 2H), 3.2 (s, 3H), 3.55 (t, 1H, J = 8.7 Hz), 7.0−7.2 (m, 5H), 9.3 (brs, 1H); ^{13}C NMR (C_6D_6) δ 178.3 (s), 140.1 (s), 129.6 (d), 127.8 (d), 126.4 (d), 97.4 (s), 51.9 (q), 45.6 (d), 40.4 (s), 39.7 (t), 25.4 (q, 3C); HRMS *m/z* calcd for $C_{15}H_{21}NO_2$ 247.1572, found 247.1570. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found C, 72.65; H, 8.60; N, 5.61.

(4*R*,5*R*/4*S*,5*S*)-5-*tert*-Butyl-4-(2-furyl)-5-methoxypyrrolidin-2-one (6b): yield 60%; mp 117−118 °C; ^{1}H NMR (C_6D_6) δ 1.1 (s, 9H), 2.5 (dd, 1H, J = 11.9, 7.0 Hz), 2.8 (dd, 1H, J = 11.9, 5.6 Hz), 3.1 (s, 3H), 3.65 (dd, 1H, J = 6.7, 5.8 Hz), 6.0 (m, 1H), 6.1 (m, 1H), 7.1 (m, 1H), 9.4 (brs, 1H); ^{13}C NMR (C_6D_6) δ 176.7 (s), 152.6 (s), 140.6 (d), 109.9 (d), 107.4 (d), 97.0 (s), 50.6 (q), 39.4 (s), 37.5 (d), 36.3 (t), 24.8 (q, 3C); HRMS *m/z* calcd for $C_{13}H_{19}NO_3$ 237.1365, found 237.1365. Anal. Calcd for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90. Found C, 65.67; H, 8.19; N, 5.83.

5-*tert*-Butyl-4-(2-furyl)-1,3-dihydro-2*H*-pyrrol-2-one (8b): yield 23%; mp 137−139 °C; ^{1}H NMR δ 1.3 (s, 9H), 3.35 (s, 2H), 6.1 (m, 1H), 6.4 (m, 1H), 7.4 (m, 1H), 8.6 (brs, 1H); ^{13}C NMR δ 178.0 (s), 149.0 (s), 146.7 (s), 141.1 (d), 110.9 (d), 107.8 (d), 102.0 (s), 41.5 (t), 32.8 (s), 28.8 (q, 3C); HRMS *m/z* calcd for $C_{12}H_{15}NO_2$ 205.1103, found 205.1104. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found C, 70.15; H, 7.24; N, 6.91.

5-*tert*-Butyl-4-phenyl-1,5-dihydro-2*H*-pyrrol-2-one (9a): yield 90%; mp 207−209 °C; ^{1}H NMR δ 0.8 (s, 9H), 4.5 (s, 1H), 6.1 (s, 1H), 7.3−7.5 (m, 5H), 8.0 (brs, 1H); ^{13}C NMR δ 173.3 (s), 163.2 (s), 135.3 (s), 129.2 (d), 128.5 (d), 127.3 (d), 124.7 (d), 68.4 (d), 35.5 (s), 26.8 (q, 3C); HRMS *m/z* calcd for $C_{14}H_{17}NO$ 215.1310, found 215.1309. Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found C, 78.25; H, 7.74; N, 6.63.

5-*tert*-Butyl-4-(2-furyl)-1,5-dihydro-2*H*-pyrrol-2-one (9b): yield 78%; mp 166−168 °C; ^{1}H NMR δ 0.9 (s, 9H), 4.4 (s, 1H), 6.2 (s, 1H), 6.5 (m, 1H), 6.6 (m, 1H), 7.5 (m, 1H), 7.6 (brs, 1H); ^{13}C NMR δ 173.6 (s), 150.5 (s), 148.5 (s), 143.6 (d), 122.2 (d), 111.8 (d), 111.4 (d), 67.9 (d), 35.6 (s), 26.6 (q, 3C); HRMS *m/z* calcd for $C_{12}H_{15}NO_2$ 205.1103, found 205.1103. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found C, 70.15; H, 7.44; N, 6.71.

[4 + 2] Cycloaddition of 2-Azadienes 1a,c and Alkynyl Fischer Carbene Complex 10a. Synthesis of 11 and 12. A mixture of 2-azadiene **1a** (1 mM) and alkynyl Fischer carbene **10a** (1 mM) in 50 mL of THF was stirred at 25 °C for 18 h. Then the solvent was removed under reduced pressure and the crude product purified by column chromatography (hexane/ethyl acetate 1:1) to give **11a** as a red solid.

A solution of compound **11a** (1 mM) in 50 mL THF was heated at 60 °C for 18 h, then the solvents were removed, and the residue was purified by column chromatography to give **12a.**

A solution of 2-azadiene **1c** (1 mM) and Fischer carbene complex **10a** (1 mM) in 50 mL of THF was stirred at 25 °C for 62 h, and solvent removal and purification by column chromatography (hexane/ethyl acetate 1:1) gave **12b**.

Pentacarbonyl[5-[6-*tert*-butyl-4-(trimethylsilyl)-3,6-dihydro-2(1*H*)-pyridinonyl]methoxymethylene]tungsten(0) (11a): yield 92%; mp 127−129 °C; IR (THF) 2069, 1934 cm^{-1}; ^{1}H NMR δ 0,1 (s, 9H), 0.8 (s, 9H), 2.95 (d, 1H, J = 21.5, 1.7 Hz), 3.15 (d, 1H, J = 21.5 Hz), 4.6 (s, 3H), 4.75 (d, 1H, J = 4.3 Hz), 7.8 (brd, 1H, J = 4.3 Hz); ^{13}C NMR δ 327.8 (s), 201.7 (s), 196.9 (s, 4C), 171.1 (s), 160.5 (s), 129.8 (s), 69.6 (q), 66.4 (d), 40.8 (s), 36.0 (t), 26.2 (q, 3C), −0.1 (q, 3C). Anal. Calcd for $C_{19}H_{25}NO_7SiW$: C, 38.59; H, 4.26; N, 2.37. Found C, 38.69; H, 4.35; N, 2.31.

6-*tert*-Butyl-4-(trimethylsilyl)-5-((*Z*)-methoxymethylene)-5,6-dihydro-2(1*H*)-pyridinone (12a): yield 82%; mp 218−220 °C; ^{1}H NMR δ 0,15 (s, 9H); 0.7 (s, 9H); 3,45 (m, 1H); 3,6 (s, 3H); 5,9 (m, 2H); 6,85 (brs, 1H); ^{13}C NMR δ 165.2 (s), 151.1 (s), 148.1 (d), 128.9 (d), 110.3 (s), 63.5 (d), 59.7 (q), 37.3 (s), 26.1 (q, 3C), −0.9 (q); HRMS *m/z* calcd for $C_{10}H_{16}NO_2Si$ (M^+ − *t*-Bu) 210.0950, found 210.0949. Anal. Calcd for $C_{14}H_{25}NO_2Si$: C, 62.87; H, 9.42; N, 5.23. Found C, 62.71; H, 9.44; N, 5.30.

6-(2-Furyl)-4-(trimethylsilyl)-5-((*Z*)-methoxymethylene)-5,6-dihydro-2(1*H*)-pyridinone (12b): yield 71%; oil; ^{1}H NMR δ 0.1 (s, 9H), 3.7 (s, 3H), 5.0 (m, 1H), 5.95 (m, 1H), 6.1 (m, 1H), 6.2 (m, 1H), 6.25 (m, 1H), 7.2 (brs, 1H), 7.3 (m, 1H); ^{13}C NMR δ 165.3 (s), 154.6 (s), 149.9 (s), 147.7 (d), 141.9 (d), 128.5 (d), 110.6 (s), 110.1 (d), 105.9 (d), 59.9 (q), 52.0 (d), 1.1 (q, 3C); HRMS *m/z* calcd for $C_{14}H_{19}NO_3Si$ 277.1134, found 277.1137. Anal. Calcd for $C_{14}H_{19}NO_3Si$: C, 60.62; H, 6.90; N, 5.05. Found C, 60.55; H, 6.97; N, 5.01.

[4 + 2] Cycloaddition of 2-Azadienes 1c−e and Alkynyl Fischer Carbene Complex 10b. Synthesis of 13. A mixture of 2-azadienes **1c**−**e** (1 mM) and alkynyl carbene **10b** (1 mM) in 50 mL of THF was stirred at 60 °C for 18 h. Then the solvent was removed under reduced pressure and the crude purified by column chromatography (hexane/ethyl acetate 3:1) to give compounds **13**.

(1*R*,9*R*/1*S*,9*S*)-1-*tert*-Butyl-9-methoxy-1,2,4,9-tetrahydro-3*H*-indeno[2,1-c]pyridin-3-one (13a): yield 76%; mp 183−185 °C; ^{1}H NMR δ 1.1 (s, 9H), 3.0 (s, 3H), 3.3 (m, 2H), 3.9 (m, 1H), 5.3 (m, 1H), 7.0 (brs, 1H), 7.1−7,4 (m, 3H), 7.5 (d, 1H, J = 7.3 Hz); ^{13}C NMR δ 170.8 (s), 142.6 (s), 141.5 (s), 137.8 (s), 136.8 (s), 128.6 (d), 126.2 (d), 123.9 (d), 118.6 (d), 83.3 (d), 61.6 (d), 52.0 (q), 38.0 (s), 29.9 (t), 26.2 (q, 3C); HRMS *m*/*z* calcd for $C_{17}H_{21}NO_2$ 271.1572, found 271.1575. Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found C, 75.07; H, 7.73; N, 5.21.

(1*R*,9*R*/1*S*,9*S*)-9-Methoxy-1-phenyl-1,2,4,9-tetrahydro-3*H*-indeno[2,1-c]pyridin-3-one (13b): yield 84%; mp 204−206 °C; ^{1}H NMR δ 3,2 (s, 3H), 3.5 (m, 2H), 4.65 (m, 1H), 5.45 (m, 1H), 6.6 (brs, 1H). 7.1−7.5 (m, 9H); ^{13}C NMR δ 168.9 (s), 142.2 (s), 141.3 (s), 140.8 (s), 136.8 (s), 134.0 (s),129.0 (d), 128.7 (d), 128.3 (d), 126.6 (d), 126.5 (d), 124.0 (d), 119.0 (d), 81.0 (d), 57.6 (d), 53.0 (q), 29.0 (t); HRMS *m*/*z* calcd for $C_{19}H_{17}NO_2$ 291.1259, found 291.1256. Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found C, 78.17; H, 5.71; N, 5.01.

(1*R*,4*S*,9*R*/1*S*,4*R*,9*S*)-1-*tert*-Butyl-9-methoxy-4-methyl-1,2,4,9-tetrahydro-3*H*-indeno[2,1-c]pyridin-3-one (13c): yield 62%; mp 199−201 °C; mp 199−201 °C; ^{1}H NMR δ 1.1 (s, 9H), 1.6 (d, 3H, J = 7.3 Hz), 3.05 (s, 3H), 3.5 (dq, 1H, J = 7.3, 3.0 Hz), 3.95 (t, 1H, J = 3.0 Hz), 5.3 (s, 1H), 6.6 (brd, 1H, J = 3.0 Hz), 7.2−7.4 (m, 3H), 7.5 (d, 1H, J = 6.9 Hz); ^{13}C NMR δ 174.0 (s), 142.8 (s), 142.3 (s), 141.2 (s), 135.1 (s), 128.6 (d), 126.1 (d), 123.9 (d), 119.0 (d), 83.3 (d), 61.8 (d), 52.1 (q), 36.2 (s), 34.9 (d), 26.6 (q, 3C), 18.0 (q). Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91. Found C, 75.57; H, 8.18; N, 4.82.

[4+3] Cycloaddition of 2-Azadienes 1c,d an Alkenyl Fischer carbene complexes 14a,b Synthesis of 2*H*-azepin-2-ones 15 and 16. A mixture of alkenyl Fischer carbene **14a,b** (1 mM) and 2-azabutadiene **1c,d** in 50 mL of THF was heated at 60 °C for 14 h. After solvent removal, the crude 1:1 mixture of **15a** and **16a** was separated by column chromatography (hexane/ethyl acetate, 1:1). Compounds **15b** and **15c** were purified by the same procedure. The diastereoisomers **16b** and **16c** were formed in very low amounts and were not isolated.

(6*R*,7*S*/6*S*,7*R*)-4-Methoxy-6,7-diphenyl-1,3,6,7-tetrahydro-2*H*-azepin-2-one (15a): yield 42%; mp 135−137 °C; ^{1}H NMR δ 3,1 (d, 1H, J = 16.8 Hz), 3.5 (s, 3H), 3.7 (m, 1H), 4.0 (m, 1H), 4.8 (m, 1H), 5.3 (m, 1H), 6.0 (brd, 1H, J = 7.4 Hz), 6.6−7.4 (m, 10H); ^{13}C NMR δ 171.6 (s), 149.1 (s), 138.0 (s), 137.5 (s), 130.1 (d), 128.2 (d), 127.7 (d), 127.5 (d), 127.1 (d), 126.5 (d), 100.1 (d), 58.4 (d), 54.3 (q), 50.6 (d), 40.0 (t); HRMS *m*/*z* calcd for $C_{19}H_{19}NO_2$ 293.1416, found 293.1420. Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found C, 77.85; H, 6.76; N, 4.61.

(6*R*,7*R*/6*S*,7*S*)-4-Methoxy-6,7-diphenyl-1,3,6,7-tetrahydro-2*H*-azepin-2-one (16a): yield 38%; mp 136−138 °C; ^{1}H NMR δ 2.9 (d, 1H, J = 15.5 Hz), 3.5 (s, 3H), 4.0 (m, 2H), 4.8 (m, 2H), 6.1 (brs, 1H), 6.8−7.4 (m, 10H); ^{13}C NMR δ 172.4 (s), 148.7 (s), 142.1 (s), 139.6 (s), 128.5 (d), 128.2 (d), 128.0 (d), 127.9 (d), 126.9 (d), 126.5 (d), 99.7 (d), 61.5 (d). 54.4 (q), 51.3 (d), 39.8 (t); HRMS *m*/*z* calcd for $C_{19}H_{19}NO_2$ 293.1416, found 293.1424. Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found C, 77.90; H, 6.49; N, 4.71.

(6*R*,7*S*/6*S*,7*R*)-7-*tert*-Butyl-4-methoxy-6-phenyl-1,3,6,7-tetrahydro-2*H*-azepin-2-one (15b): yield 94%; mp 144−146 °C; ^{1}H NMR δ 0,8 (s, 9H), 3.0 (d, 1H, J = 16.8 Hz), 3.4 (s, 3H), 3.7−3.9 (m, 3H), 4.6 (d, 1H, J = 3.9 Hz), 5.6 (brd, 1H, J = 8.2 Hz), 7.2 (m, 5H); ^{13}C NMR δ 172.1 (s), 147.7 (s), 140.6 (s), 129.6 (d), 128.1 (d), 126.9 (d), 102.5 (d), 62.1 (d), 54.1 (q), 44.0 (d), 39.9 (t), 33.8 (s), 27.2 (q, 3C); HRMS *m*/*z* calcd for $C_{19}H_{23}NO_2$ 273.1729, found 273.1726. Anal. Calcd for $C_{19}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found C, 74.55; H, 8.66; N, 5.03.

(6*R*,7*S*/6*S*,7*R*)-7-*tert*-Butyl-6-(2-furyl)-4-methoxy-1,3,6,7-tetrahydro-2*H*-azepin-2-one (15c): yield 88%; mp 139−141 °C; ^{1}H NMR δ 0.8 (s, 9H), 2.9 (d, 1H, J = 16.3 Hz), 3.4 (s, 3H), 3.6 (dd, 1H, J = 9.0, 1.7 Hz), 3.75 (m, 1H), 3.95 (m, 1H), 4.6 (m, 1H), 5.7 (brd, 1H, J = 9.0 Hz), 6.05 (m, 1H), 6.15 (m, 1H), 7.25 (m, 1H); ^{13}C NMR δ 172.1 (s), 153.5 (s), 148.9 (s), 140.4 (d), 110.8 (d), 108.1 (d), 99.6 (d), 61.5 (d), 54.2 (q), 39.8 (t), 37.3 (d), 33.3 (s), 26.7 (q, 3C); HRMS *m*/*z* calcd for $C_{15}H_{21}NO_3$ 263.1521, found 263.1517. Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found C, 68.35; H, 8.19; N, 5.49.

Tautomerization of 2*H*-Azepin-2-ones 15b,c. Synthesis of 17. A solution of azepin-2-ones **15b**,**c** (0.5 mM) in 30 mL of THF was treated with 2 M NaOH (30 mL). Stirring was continued for 3 h at room temperature, and then the reaction was treated with ice−water and extracted with ether (3 × 20 mL). The combined organic layers were concentrated at reduced pressure to give crude azepin-2-ones **17**, which were purified by column chromatography (ethyl acetate/hexane, 4:1).

(6*R*,7*S*/6*S*,7*R*)-7-*tert*-Butyl-4-methoxy-6-phenyl-1,5,6,7-tetrahydro-2*H*-azepin-2-one (17b): yield 95%; mp 158−160 °C; ^{1}H NMR δ 0.7 (s, 9H); 2.5 (ddd, 1H, J = 14.6, 7.3, 2.2 Hz), 2.9 (dd, 1H, J = 14.6, 10.3 Hz), 3.45 (m, 1H), 3.55 (m, 1H), 3.7 (s, 3H), 5.1 (d, 1H, J = 2.2 Hz), 5.9 (brd, 1H, J = 5.6 Hz), 7.1−7.4 (m, 5H); ^{13}C NMR δ 173,1 (s), 167.6 (s), 142.0 (s), 128.9 (d), 128.3 (d), 127.2 (d), 95.2 (d), 65.1 (d), 55.5 (q), 48.3 (d), 41.2 (t), 33.8 (s), 27.4 (q, 3C); HRMS *m*/*z* calcd for $C_{17}H_{23}NO_2$ 273.1729, found 273.1727. Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found C, 74.70; H, 8.39; N, 5.17.

(6*R*,7*S*/6*S*,7*R*)-7-*tert*-Butyl-6-(2-furyl)-4-methoxy-1,5,6,7-tetrahydro-2*H*-azepin-2-one (17c): yield 93%; mp 126−128 °C; ^{1}H NMR δ d 0.7 (s, 9H), 2.4 (dd, 1H, J = 15.0, 6.9 Hz), 2.85 (dd, 1H, J = 15.0, 9.5 Hz), 3.35 (dd, 1H, J = 6.9, 3.9 Hz), 3.55 (m, 1H), 3.6 (s, 3H), 5.1 (s, 1H), 5.8 (brd, 1H, J = 6.9 Hz), 6.1 (m, 1H), 6.2 (m, 1H), 7.1 (m, 1H); ^{13}C NMR δ 171.8 (s), 166.6 (s), 153.7 (s), 140.7 (d), 110.3 (d), 107.4 (d), 95.6 (d), 63.9 (d), 55.3 (q), 40.0 (d), 38.1 (t), 33.2 (s), 26.6 (q, 3C); HRMS *m*/*z* calcd for $C_{15}H_{21}NO_3$ 263.1521, found 263.1517. Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found C, 68.46; H, 8.14; N, 5.28.

Hydrolysis of 2*H*-Azepin-2-ones 15b,c. Synthesis of 18. To a solution of azepin-2-one **15b,c** (0.5 mM) in 30 mL of THF was added 30 mL of 3 M HCl. After stirring for 1.5 h the mixture was treated with ice−water and extracted with ether (3 × 20 mL). The combined organic layers were concentrated at reduced pressure, and the crude product was purified by column chromatoghaphy (ethyl acetate/hexane, 4:1) to give **18** as white solids.

(6*R*,7*S*/6*S*,7*R*)-7-*tert*-Butyl-6-phenyltetrahydro-3*H*-azepine-2,4-dione (18b): yield; 94%: mp 126−128 °C; ^{1}H NMR δ 0.8 (s, 9H), 2.75 (dd, 1H, J = 11.5, 6.3 Hz), 3.1 (dd, 1H, J = 11.5, 10.0 Hz), 3.3−3.7 (m, 4H), 6.55 (brd, 1H, J = 5.0 Hz), 7.1−7.4 (m, 5H); ^{13}C NMR δ 204.4 (s), 170.0 (s), 139.5 (s), 128.8 (d), 128.4 (d), 127.7 (d), 63.6 (d), 50.8 (t), 50.2 (t), 46.8 (d), 34.2 (s), 27.0 (q, 3C); HRMS *m*/*z* calcd for $C_{16}H_{21}NO_2$ 259.1572, found 259.1574. Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found C, 74.18; H, 8.15; N, 5.37.

(6*R*,7*S*/6*S*,7*R*)-7-*tert*-Butyl-6-(2-furyl)tetrahydro-3*H*-azepin-2,4-dione (18c): yield 96%: mp 129−131 °C; ^{1}H NMR δ 0.8 (s, 9H), 2.65 (dd, 1H, J = 12.0, 6.9 Hz), 3.15 (m, 1H), 3.35 (m, 2H), 3.6 (m, 2H), 6.05 (brd, 1H, J = 7,7 Hz), 6.15 (m, 1H), 6.3 (m, 1H), 7.35 (m, 1H); ^{13}C NMR δ 203.6 (s), 169.6 (s), 151.9 (s), 141.6 (d), 110.5 (d), 108.0 (d), 63,1 (d), 50.9 (t), 47.5 (t), 39.5 (d), 33.7 (s) 26.4 (q, 3C); HRMS *m*/*z* calcd for $C_{14}H_{19}NO_3$ 249.1365, found 249.1369. Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found C, 67.61; H, 7.68; N, 5.54.

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